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(54) ROOM TEMPERATURE-SETTING COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a room temperature-setting composition which contains an organic polymer having at least one reactive silicon-containing group as the main component and has a sufficient adhesiveness even to the steel plate coated with an acrylic resin or with a fluororesin by an electrophoretic deposition process, or to the cured product of a sealant such as a silicone sealant.

SOLUTION: This room temperature-setting composition comprises (A) 100 pts. mass of an organic polymer which has at least one silicon-containing group, has a hydroxyl group or a hydrolyzable group bonding to the silicon, and can crosslink by forming a siloxane bond, (B) 1-50 pts. mass of an epoxy resin, (C) 0.1-30 pts. mass of an oxazolidine compound, (D) a silanol condensation catalyst, and (E) an amine promoter.

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. sss shows the word which can not be translated.

3. In the drawings, any words are not translated.

CLAIMS

[Claim(a)]

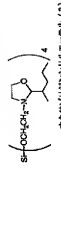
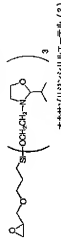
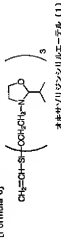
[Claim 1] (A) Organic polymer 100 mass part which has a hydroxyl group or a hydrolytic basis combined with a silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond, (B) A room-temperature-curing nature constituent containing one to epoxy resin 50 mass part, the (C) oxazolidone compound (1) - 30 mass part, the (D) silanol condensation catalyst, and (E) amine compound or catalyst (12) - 20 mass part, and (F) a room-temperature-curing nature constituent containing at least one of (1) ORUTOGI acid ester, (2) The room-temperature-curing nature constituent chosen from a group which consists of a mixture or addition of ORUTOGI acid ester and (3) ORUTOGI acid ester, and a p-toluenesulfonic-acid monoisocyanate according to claim 1.

[Translation done.]

gamma-glycidyloxy propyltriethoxysilane. By making a titanium alkoxide, aluminum alkoxide, or divalent Sn into a catalyst, this reaction is 40 ** - 160 **, and is especially performed at 80 ** - 140 ** preferably.

[0043]The example of oxazoline allyl ether is shown below.

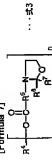
[Formula 6]



[0039]Carbonate oxazoline etc. from which carbonate oxazoline is obtained by a method of JP-H6-117252A, for example are mentioned. Hydroxyalkyl oxazoline and diaryl carbonate, such as the hydroxyalkyl oxazoline (1) above-mentioned [carbonate oxazoline], for example, it can obtain by mixing carbonate, such as dimethyl carbonate and dipropylene carbonate, react using polyhydric alcohol, such as a diethylene glycol and glycerin. 60-160 ** of this reaction is preferably performed at temperature of the range of 100-140 **, for example under existence of transesterification catalysts, such as sodium methylate. As for an addition of a catalyst, it is preferred that it is 50-1000 ppm to the total quantity of hydroxyalkyl oxazoline, carbonate, and polyhydric alcohol.

[0040]In this way, carbonate oxazoline prepared is expressed with the following formula 3.

[Formula 7]

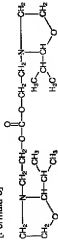


(n is an integer of 1-10 among a formula, and R¹ and R³ are the organic groups of 1-8 carbon numbers independently respectively.) R² and R³ are a hydrogen atom or an organic group of 1-8 carbon numbers independently respectively.

The following carbonate oxazoline (1) is among one example of a compound expressed with the formula 3.

[0041]

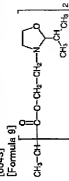
[Formula 8]



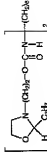
[0042]As ester oxazoline, various ester oxazoline, such as ester oxazoline obtained by the method of the US361923B gazette and the US413845B gazette, can be used, for example. For example, it can obtain by a reaction with low-grade alkyl ether of above-mentioned hydroxyalkyl

oxazoline (1), dicarboxylic acid, or polycarboxylic acid. Specifically, the following ester oxazoline (1) is mentioned. Commercial items, such as the Hardener OZ by a Bayer company atom by the following ester oxazoline (2), can also be used

[0043]



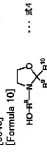
オキソゾリンエーテル (1)



オキソゾリンエーテル (2)

[0044]May use the oxazoline compound which has three or more oxazoline rings into one molecule, and this compound, it compounds as a compound which has three or more oxazoline rings in one molecule by reacting N-hydroxyalkyl oxazoline and the polycarbonate compound which are expressed with the following formula 4.

[0045]



[Formula 10]

[0046]R¹ is a divalent aliphatic hydrocarbon group which has the straight chain shape or the branched chain of the carbon numbers 2-3, for example, shows an alkylene group, an alkynylene group, and an alkynylene group here. R² and R³ show the univalent hydrocarbon group of a hydrogen atom or the carbon numbers 1-20 independently respectively. N-hydroxyalkyl oxazoline expressed with the above-mentioned formula 4 is compounded by a method more publicly known than corresponding aldehyde or ketone, and N-hydroxy alkylamine.

[0047]As aldehyde, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, 2-methylbutyraldehyde, 3-methylbutyraldehyde, hexylaldehyde, 2-methylhexylaldehyde, benzaldehyde, aliphatic aldehyde, such as octyl aldehyde and 3,5-dimethylhexylaldehyde; aromatic aldehyde, such as isopropylbenzaldehyde, trimethylbenzaldehyde, benzaldehyde, benzaldehyde, and dimethylbenzaldehyde; isobutyraldehyde, isobutyraldehyde, 2-methylbutyraldehyde, and 3-methylbutyraldehyde; etc. are preferred. As ketone, acetone, methyl isobutyl ketone, methyl isopropyl ketone, methyl isooctyl ketone, a diethyl ketone, methyl butyl ketone, methyl isobutyl ketone, methyl-tert-butyl ketone, diisobutyl ketone, cyclopentanone, cyclohexanone, etc. are preferred.

[0048]As N-hydroxy alkylamine, bis-N-(2-hydroxyethyl) amine, bis-N-(2-hydroxypropyl) amine, and N-(2-hydroxyethyl)-N-(2-hydroxypropyl) amine are preferred.

[0049]Although above-mentioned aldehyde or ketone, and hydroxy alkylamine react with this molar quantity of nitrogen corresponding to the number of mole of aldehyde or ketone, it is preferred to use aldehyde or ketone superfluously in 1.01-1.5. It is the range of 1.01-1.1 especially preferably. It is because separation with output is difficult for N-hydroxy alkylamine with this unreacted Reagen, and it becomes a cause of a fall of storage stability in order to react to an isocyanate.

[0050]As for reaction temperature, it is desirable in solvents, such as toluene and xylene, to carry out under flowing-back conditions. As for reaction time, it is desirable to consider it as 6 to 24 hours, and

it is desirable to consider it as 8 to 12 hours especially. A Reason for having made reaction time into this range is that a reaction mixture will color in less than 6 hours if it is because the reaction is imperfect and exceeds 24 hours. It is preferred to perform a reaction in the usual atmosphere. N-hydroxyalkyl oxazolidine which distills off under decomposition of superfluids is aldehyde or ketone, and is followed with the above-mentioned formula. After ending reaction is obtained.

[illegible]

[0052] An oxazolidine compound which has three or more oxazolidine rings in one molecule is compounded by making a polyisocyanate compound react to N-hydroxyalkyl oxazolidine expressed with the formula 4 under ordinary pressure with reaction temperature of 50 °* - about 100 °*.

Solvents, such as toluene and xylene, may be used in order to lower viscosity in the case of

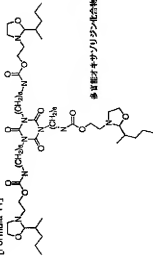
connection

composition. A quantitative ratio of N-hydroxyalkyl oxazolidine and a poly(isocyanate) compound is good for a poly(isocyanate) compound to make it react at 1 mol per 1 mol of hydroxyl of N-hydroxyalkyl oxazolidine.

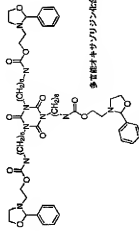
[0054]As an example of a compound of having three or more oxazolidine rings, the polyfunctional oxazolidine compound (1), (2) expressed with a following formula is mentioned to such one molecule.

[0055]

[Formula 11]



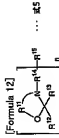
鳥宮龍太郎サノリジン化合物 (1)



東京館オホサノリジン化合物(2)

[0055] As other examples of an isocyanate oxazolidine compound, the compound expressed with the following formula 5 can be shown.

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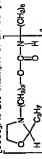


[Formula 12]

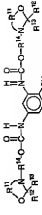
[0058] here— R^{11} —the carbon numbers 2–6—desirable—the carbon numbers 2–3—more—desirable—the allylene group of the carbon number 2—it, R^{12} and R^{13} are a hydrogen atom, a desirable—the allylene group of one or more allyl group, an allylic alkyl group of the carbon numbers 5–7, with a carbon numbers of one or more allyl group, an allylic alkyl group of the carbon numbers 5–7, or an aryl group of the carbon numbers 6–10 independently, respectively. As for R^{14} , it is preferred that it is an aryl group including the allylene group of the carbon numbers 2–6, an aryl group, the allylene group of the carbon numbers 2–6, an allyl group, the allylene group of the carbon numbers 2–6 including a urethane bond, or a urethane bond, and the allyl group or second group of the carbon numbers 1–5 which has a urethane bond.

[0053] It is a basic objective by removing an isocyanate group from polyisocyanates, and should be noted that the removal of the isocyanate group from a polyisocyanate compound results in a compound used as the just form the skeleton of an isocyanate compound. It is preferred that it is a compound used as the just form the skeleton of an isocyanate compound, n is an integer of 1-4 and it is preferred that the skeleton of diisocyanate or tri-isocyanate compound, n is an integer of 1-4 and it is preferred that the skeleton of diisocyanate or tri-isocyanate compound, which was able to balance tensile strength and a tensile piece of expansion especially as n is 2 or 3 is obtained. If 3 is exceeded, it will become it is hard and weak, and if n is 2 or 3, The hardened material will become insufficient if it is less than two.

[0060] As the example of an isocyanate oxazolidine compound, [Formula 13]



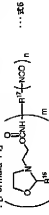
イソシアネートオキサゾリジン化合物 (1)



イハニマキニトナホクノリハナホク (2)

Polyfunctional oxazolidine, such as which TDI base, a MDI base, a XDI base, and a HDI base, etc. are mentioned and commercial items, such as the Bayern hardener OZ, can be used.

[0061] Other examples with a preferred isocyanate oxazolidine compound are the following formulas 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839



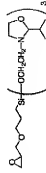
(as for R^{16} , the integer of 1-8 and n of the residue and m which are obtained from organic polyisocyanate except for an isocyanate group as for five or more aliphatic hydrocarbon groups with a number of carbon atoms, and R^{17} are the integers of 0-4 among a formula.) — It is an oxazolidine compound shown.

[0022]As for R¹⁶, five or more carbon atom numbers are an aliphatic hydrocarbon group with 5-15 carbon atoms preferably among the above-mentioned formula. For example, n-pentyl, 2-methylpentyl, 3-methylpentyl, 3,5,5-trimethylpentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, etc. are mentioned. Especially, a carbon with 5-10 carbon atoms is preferred. And substitution of hydrolysis of a position of R¹⁶ is [both substituents] too quick in aliphatic hydrocarbon, and storage stability is bad. Hydrolysis is slow in R¹⁶ being an aromatic group.

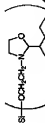
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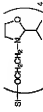
オキサゾリジンシリルエーテル化合物 (1)



オキサゾリジンシリルエーテル化合物 (2)



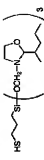
オキサゾリジンシリルエーテル化合物 (3)



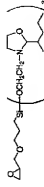
オキサゾリジンシリルエーテル化合物 (4)

[0076]

[Formula 18]



オキサゾリジンシリルエーテル化合物 (5)



オキサゾリジンシリルエーテル化合物 (6)



オキサゾリジンシリルエーテル化合物 (7)

[0077] The oxazolidine compound furthermore suitably used as an ingredient (C) of this invention is a compound shown with the following formula 19.

[Formula 19]



[0078] R^{2a} is an aliphatic hydrocarbon group which has with a carbon numbers of one or more straight chain shape or branched chain, for example, shows an alkyl group, an alkenyl group, and an aralkenyl group here. R^{2b} and R^{2c} show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-20 independently respectively. These desirable examples are shown below.

[0078]

[Formula 20]

placed about 1 cm in diameter in the shape of a bead, and cure of health 50 °± 20 ° for three days and for three days was performed. Then, it is based on the simple adhesive property examination (Japanese material industrial meeting structural sealing material handbook p.103) by info cutting, and is friction test ***** (a 0-degree friction test and a 90-degree friction test about a 0 degree direction and a 90-degree direction as a tensile direction. The adhesive property was evaluated like Oxazolidine destruction, **thin layer exfoliation, and interface exfoliation.

[0107]A result is shown in the 3rd table. The room-temperature-curing nature constituent (working example 1 and 2) of this invention reveals the outstanding adhesive property as a which, adhering to glass, an acrylic deacrylating resin, etc., and the hardened steel plate, and a silicone series resin (hardened resin) and a clear resin, the 3rd table. When using the primer (primer B) inferior with exfoliation nature, the outstanding adhesive property can be made to reveal by adding (F) oxazolidine ring breakage accelerator further, or choosing the suitable (C) oxazolidine compound. On the other hand, the conventional room-temperature-curing nature constituent (comparative example 1) which contains (A) organically polymer and the (B) epoxy resin, and does not contain the (C) oxazolidine compound does not reveal sufficient adhesive property.

[0108]

[Table 3]

第 3 表

室温硬化性組成物	比較例						
	1	2	3	4	5	6	7
プライマー組成物	A	A	B	B	B	B	B
はく離試験 (90°はく離/0°はく離)							
アルミニウム板	O/x	O/O	O/x	O/Δ	O/Δ	O/O	O/O
ガラス板	O/x	O/Δ	O/O	O/x	O/Δ	O/O	O/O
アクリル系接着剤	Δ/x	O/Δ	O/O	Δ/x	Δ/Δ	O/Δ	O/O
フタ素体付板	Δ/x	O/Δ	O/O	Δ/x	Δ/x	O/O	O/O
シリコーン系シーラント硬化剤	—	—	x/x	Δ/x	Δ/x	Δ/Δ	Δ/O

[0109]

[Effect of the Invention]The room-temperature-curing nature constituent of this invention reveals sufficient adhesive property also to the hardened material of sealant, such as a difficulty adhesive property steel plate in which acrylic electropainting, fluoride paint, etc. were performed, and silicone series sealant.

[Translation done.]